NEAR ULTRAVIOLET ABSORPTION SPECTRUM OF β-BROMOSTYRENE

KAMALESH SINGH AND V. B. SINGH

DEPARTMENT OF SPECTROSCOPY, BANARAS HINDU UNIVERSITY,

VARANASI-5, INDIA.

(*Received August* 7, 1968; *Resubmitted December* 21, 1968)

(Plate 17)

ABSTRACT. The near ultraviolet absorption spectrum of β-bromostyrene vapour has been recorded. Fortyfive red degraded bands in the region 2700–3000 A have been measured and analysed. The (0,0) band has been identified at 34374 cm^{-1}. The vibrational analysis has been proposed in terms of 192 and 246 cm^{-1} ground state and 175, 238, 692 and 1123 cm^{-1} excited state frequencies.

INTRODUCION

The spectral study of styrene is important for the reason that CH : CH_2 group is neither *o*-, *p*- nor meta directing. In β-bromostyrene due to substitution of bromine atom in β-position the spectrum of styrene is modified and extent of modification is a measure of the strength of perturbation caused by bromine atom. This provides an electronic characterization of the group. Therefore a study of this molecule has been made in the present investigation.

EXPERIMENTAL

The absorption spectrum has been recorded with the cell length, 25, 50, 75, and 100 cm and the container of the liquid was kept at various temperatures ranging from −15°C to 34°C. The chemical was obtained from Eastman Kodak Company and was distilled before use. The same technique was adopted as by Singh (1966). The time of exposure varied from half an hour to one hour.

RESULTS AND DISCUSSION

The absorption spectrum of this molecule (figure 1.) consists of about fortyfive bands lying in the region 2700–3000A. Some of the bands are sharp and clearly degraded towards red while others are broad and diffuse. At temperature greater than 30°C the bands at shorter wavelength side get more and more diffuse till a continuous absorption sets in. The different plates have been measured and analysed. Sharp bands are expected to be accurate upto ±5 cm^{-1} while for diffuse bands this may be somewhat higher. The wavenumber and their visual estimated intensities are presented in table I along with assignments proposed.

The molecule β-bromostyrene belongs the C_s point group if we assume the (CH : CHBr) group to behave as a single particle. The electronic transition for

Indian Journal of Physics
Vol. 42 No. 11
PLATE - 17

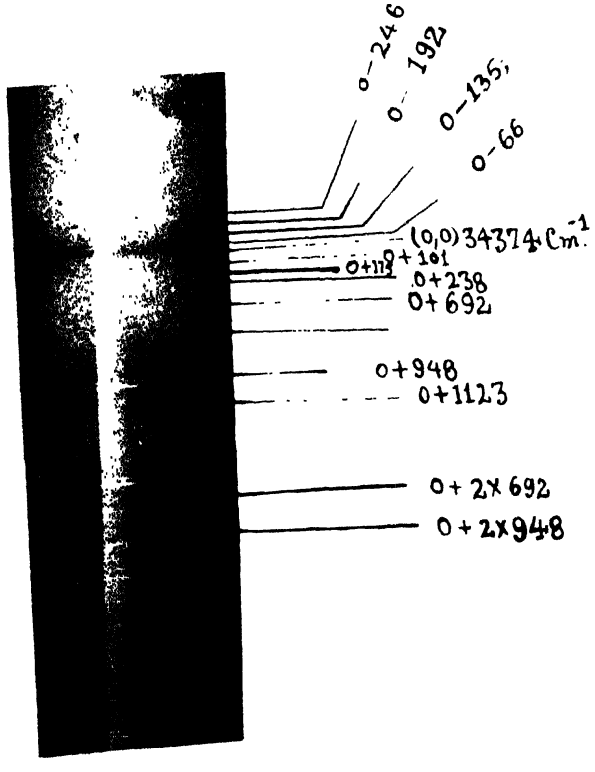

Figure 1. Near ultraviolet absorption spectrum of β - Bromostyrene.

the absorption system which corresponds to the forbidden 2600 A system of benzene can then be taken as A′—A′. This is an allowed transition and the spectrum shows the characteristic of an allowed transition.

The ultraviolet absorption of styrene has been studied by Lay (1918) and Robertson (1950) who identified the (0,0) band with strong intensity at 34761 cm^{-1}. On substitution of the bromine atom in group in β-position, it is expected that the position of the (0,0) band would shift to the red. In our spectrum the most intense band is fround at 34374 cm^{-1} and has been identified (0,0) band. Its strong intensity is in agreement with that one would expect on the basis of Frank Condon principle for an allowed transition. There is a strong band at a separation of 948 cm^{-1} from the (0,0) band. This separation has been taken as an excited state fundamental which is observed in a band at 36274 cm^{-1}. Many other prominent bands in the spectrum may be explained by this frequency in combination with other excited state fundamentals. The corresponding ground state frequency has not been observed in the absorption spectrum but it can probably be correlated with the weakly observed infrared frequency 1006 cm^{-1} (Singh, 1968). This excited state frequency may be assigned to the ring breathing mode. This is in agreement with the well known observation that the magnitude of the ring breathing frequency in mono-substituted benzene is nearly 1000 cm^{-1}.

Another excited state fundamental of magnitude, 1123 cm^{-1}, is observed in a medium strong band at 35497 cm^{-1}. The second quantum of this frequency is involved in a weak band at 36592 cm^{-1}. It has been correlated with the ground state frequency 1221 cm^{-1} observed in the infrared with strong intensity. Combination of this frequency with other excited state fundamentals at 238, 692, 948 cm^{-1} have also been observed. This frequency has been assigned to C–X stretching mode. This assignment is supported by the assignment made by Tripathy (1967) in the case of three isomeric chlorostyrene and by Ansari (1967) in the case of three isomeric bromostyrenes.

A medium strong band at 35066 cm^{-1} to the shorter wavelength side of the (0,0) band has been measured at a separation of 692 cm^{-1}. This involves an excited state frequency. The second quantum of this frequency is involved in a weak band at 35744 cm^{-1} which corresponds to the 703 cm^{-1} b_{2g} vibration of benzene. This frequency may be assigned to the C–C–C out-of-plane bending mode corresponding to 699 cm^{-1} vibration of styrene. In isomeric bromostyrene this frequency has been found at somewhat higher value (Ansari, 1968). The pair of the bands 34549 and 34612 cm^{-1} involves a separation of 175 and 238 cm^{-1} from the (0,0) band respectively which have been taken as the excited state frequency of the molecule. These excited state frequencies may be correlated with the ground state frequencies at 192 and 246 cm^{-1}. These excited state frequencies have been observed to combine with many excited state frequencies and may be assigned to the C–Br out-of-plane and in-plane bending modes respectively.

The correspondence between the various ground and excited state frequencies of the molecule is given in table 2.

Table 1. Near Ultraviolet Absorption Bands of β-Bromostyrene

Wavenumber (cm^{-1})	Intensity	Assignment
34128	2	0−246
34182	3	0−192; 0−3×66
34229	5	0−135; 0−2×66
34308	6	0−77
34347	7	0−27
34374	10s	0−0
34407	5	0+33
34475	6	0+101
34549	5	0+175
34612	4	0+238
34677	3	
34743	1	
34797	1	0+175+238
35066	5	0+692
35080	3	0+948−246
35116	4	0+948−192; 0+742
35185	3	0+948−135
35257	4	0+948−66
35295	5	0+948−27
35322	8s	0+948
353556	6	0+948+33
35441	3	0+948+101
35497	4	0+1132
35512	2	0+2×692−246
35561	2	0+948+233; 0+2×692−192
35591	1	0+1123+101
35616	2	0+2×692−135
35683	2	0+2×692−66; 0+1123+175
35744	2d	0+2×692; 0+1123+238
35788	1	0+2×692+33
35936	1	0+2×692+175
36016	1	0+692+948
36204	1	0+2×948−66
36274	2d	0+2×948
36305	1	0+2×948+33
36455	1	0+2×948+175; 0+948+1123
36479	1	
36630	1d	0+2×1123−27
36630	1d	0+2×1123
36710	1	0+2×692+948
36854	1	0+2×1123+238
36885	1	0+2×692+1123

s = sharp; d = diffuse.

Table 2. Fundamental vibrational frequencies of β-bromostyrene

Infrared		Absorption spectrum				Assignments
cm^{-1}	(Int.)	Ground state	(Int.)	Excited state	(Int.)	
		192	(3)	175	(5)	C–Br o.p. bending
		246	(2)	238	(4)	C–Br i.p. bending
				692	(5)	C–C–C o.p. bending
1006	(2)			948	(8)	C–C stretching (ring breathing)
1221	(8)			1123	(4)	C–X stretching

o.p. = out-of-plane; i.p. = in-plane and X = CH : CHBr.

ACKNOWLEDGMENTS

The authors express their thanks to Prof. N. L. Singh and Dr. D. K. Rai for their helpful discussion. One of us (K.S.) is also grateful to U.G.C. for financial help.

REFERENCE

Ansari, B. J., 1969, *Ind. J. Pure and Appl. Phys.*, **6**, 89.
Ley, H., 1918, *Ber. Dtsch. Chem. Ges.*, **51**, 1808.
Nagakura, S. and Tanaka, J., 1954. *J, Chem. Phys.*, **22**, 236.
Robertson, W. W., Music, J. F., and Matson, F. A., 1950, *J. Am. Chem. Soc.*, **72**, 5260.
Singh, K. and Singh, V. B., 1968, *Current Science*, **37**, 525.
Singh, V. B. and Singh, I. S., 1966, *Mole. Spectroscopy*, **20**, 282.
Tripathi, G. N. R., 1967, *Ph.D. Thesis*, Gorakhpur University.